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Leaf Alcohol XXI[1]: Photochemical and Thermal Isomerization among Leaf Aldehyde and its Isomers

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Irradiation of a 0.1 M solution of *E*-hex-2-en-1-al in ether with a 100 W high-pressure mercury lamp under nitrogen yielded a photostationary mixture of *E*-hex-2-en-1-al, *Z*-hex-2-en-1-al and *Z*-hex-3-en-1-al (25:15:60). The mechanism of isomerization of *E*-hex-2-en-1-al to *Z*-hex-2-en-1-al *via* *Z*-hex-3-en-1-al was suggested.

INTRODUCTION

Leaf alcohol, *Z*-hex-3-en-1-ol, and leaf aldehyde, *E*-hex-2-en-1-al (I), which are responsible for a characteristic fresh green leaf odor, are widely distributed in green leaves of shrubs, in fruits and vegetables, accompanied by other related alcohols, *E*-hex-2-en-1-ol, *Z*-hex-2-en-1-ol and *Z*-hex-3-en-1-ol.[2]

The recent findings, that lipoxygenase isolated and purified from tea seeds catalyzed to convert linolenic acid to 13-hydroperoxyoctadeca-*Z*-9,15-*E*-11-trienolic acid, a precursor of *Z*-hex-3-en-1-al (III),[3] and that an alcohol: NAD oxidoreductase isolated from each of fresh tea leaves and tea seeds catalyzed the reduction of (I) to *E*-hex-2-en-1-ol,[1] suggest that the interconversion among the precursor aldehydes such as (I), *Z*-hex-2-en-1-al (II) and (III) may play important roles in biosynthesis of hexenols including leaf alcohol.[1]

This paper deals with the photochemical and thermal isomerization reactions in systems involving these aldehydes, which may provide some non-enzymatic models for their interconversion *in vivo*.

In photochemical isomerization, irradiation of a 0.1 M solution of (I)[4] in ether with a 100 W high-pressure mercury lamp (quartz filter) under nitrogen for 60 hr yielded a photostationary mixture of (I), (II) and (III) (25:15:60).[5] The isomerization products were identified by comparison with authentic sample[6] by gas chromatography. The reaction was followed as a function of time giving the result as shown in Fig. 1. The figure clearly indicates that the isomerization of (I) to (III) proceeds *via* (II) as illustrated in scheme 1. According to this scheme, (II) initially formed by the α,β-isomerization of (I) abstracts a γ-hydrogen atom from its excited state to give an enol intermadiate (a) which isomerizes to (III) or reverts to (II). Such a mechanism has been formulated for the photochemical deconjugation of α,β-unsaturated ketones,[7] carboxylic acids and esters.[8] To the best of our knowledge, there is only one example of the photochemical deconjugation of α,β-unsaturated aldehyde in which crotonaldehyde isomerizes to but-3-en-1-al in the gas phase but not in solution.[9] The photochemical

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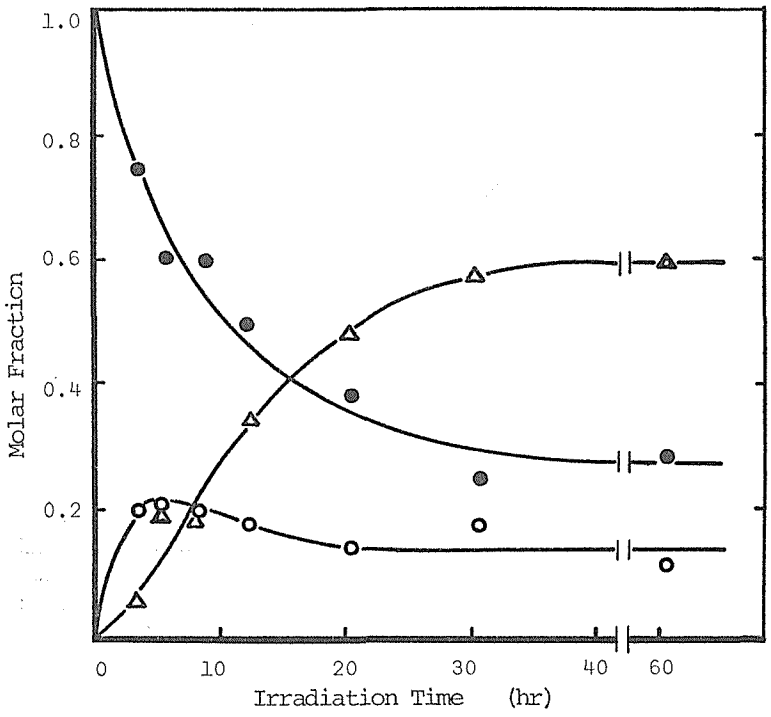
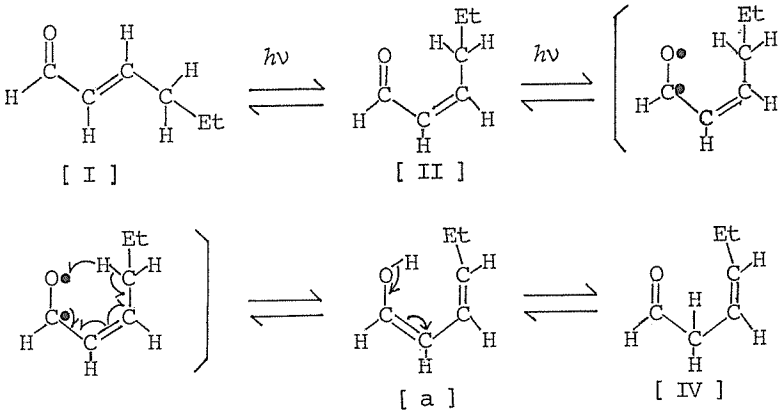


Fig. 1. Photochemical isomerization of [I]
●: [I], ○: [II], △: [III]



Scheme 1. Isomerization Mechanism of *E*-hex-2-en-1-al to *Z*-hex-3-en-1-al

equilibration between (I) and (II) was established by a following experiment. When a mixture of (I) and (II) (47:53) was irradiated under the same conditions and the product distribution was followed as a function of time, the rapid increase of (I) at the expense of (II) was observed in the earlier stage of the reaction as shown in Fig. 2. The formation of a photostationary mixture of (I), (II) and (III) suggests that the photochemical isomerization of (III) to (I) or (II) should occur. The possibility of the thermal isomeri-

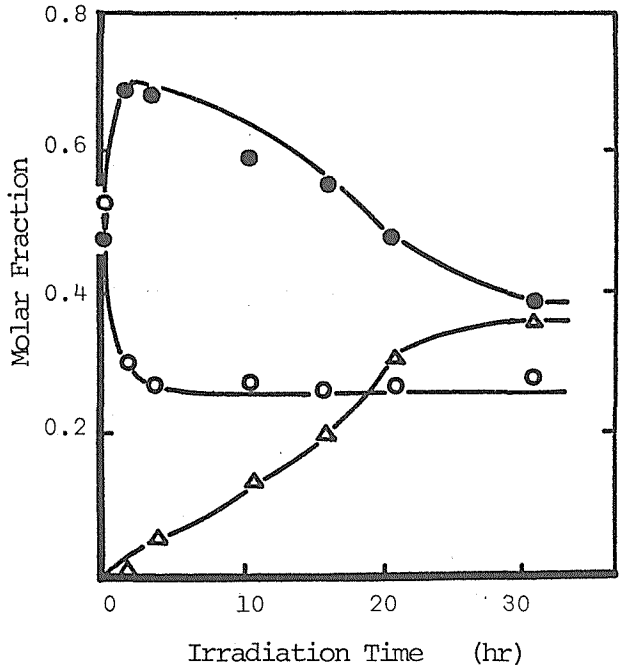


Fig. 2. Photochemical isomerization of mixture of [I:47] and [II:53], ●: [I], ○: [II], △: [III]

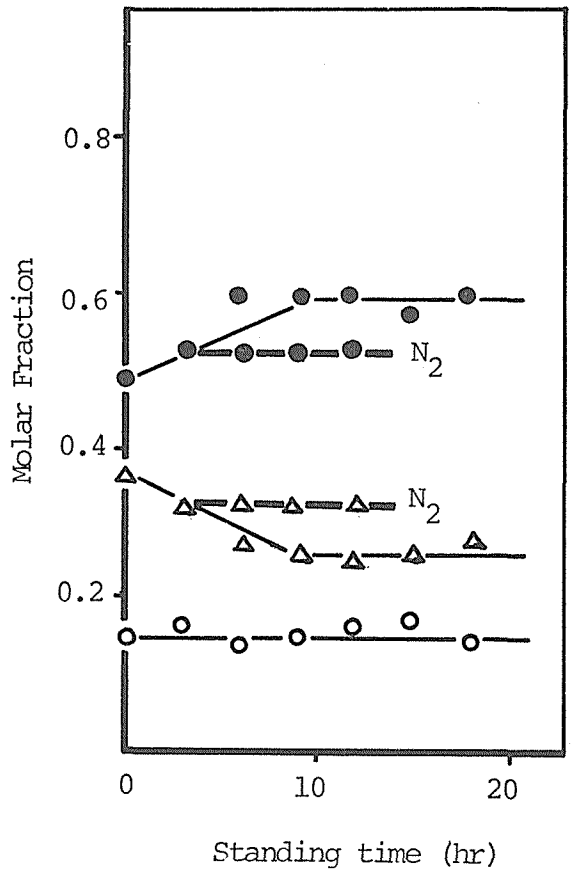


Fig. 3. Thermal isomerization of (I) to (II) *via* (III)
●: [I], ○: [II], △: [III]

zation of (III) to (I) or (II) during irradiation seems unlikely, because (III) isomerized thermally to (I) only under air but not under nitrogen as shown in Fig. 3.

EXPERIMENTAL

1. Materials

i) *E*-hex-2-en-1-al (I)

Propyl-β-chlorovinylketone. Aluminum chloride powder (13.2 g: 0.1 mole) was added to *n*-butyric acid (107 g: 1.0 mole) in 400 ml of absol. carbon tetrachloride. Under stirring and cooling at 0 °C, the dried pure acetylene gas was introduced into the mixture, and then additional 100 g of aluminum chloride powder (0.9 mole) was added to the mixture in three 30 g-portions during an hour below +5 °C. After introduction of acetylene gas for further 7 hr, the reaction mixture was slowly poured into 1500 ml of sat. NaCl ice–water. The water layer was extracted four times with 100 ml portions of ether. The extracted ether solution was combined with the carbon tetrachloride solution and it was dried over Na_2SO_4. After evaporating the ether and carbon tetrachloride, propyl-β-chlorovinylketone was obtained, bp. 80 °C/34 mm, $n_D^{16.8}$ 1.4642; yield 97.5 g; 73.2%.

β-Oxo-β-hexenal-dimethylacetal. Propyl-β-chlorovinylketone (60 g: 0.45 mole) in 100 ml of methanol was cooled below −10 °C and under vigorous stirring and cooling at 0—10 °C, methanolic sodium hydroxide solution (0.6 mole NaOH in 200 ml of methanol) was dropwise added to the mixture. Stirring was continued for an additional hour at +5 °C, and then the reaction mixture was poured into sat. NaCl ice–water. The water layer was extracted four times with 75 ml-portions of ether. After drying the ether solution over Na_2SO_4 and evaporating ether, the dimethylacetal was obtained, bp. 88–91 °C/16 mm, n_D^{19} 1.4230; yield 54.3 g; 78.0%.

E-hex-2-en-1-al. The dimethylacetal (50 g; 0.3 mole) in 150 ml of absol. ether was dropwise added to 400 ml of ether solution suspended with 3.8 g of lithium aluminum hydride under vigorous stirring, and then the solution was mildly refluxed for additional 2 hr. The reaction mixture was hydrolyzed with 2N HCl solution and was extracted with ether. After drying over Na_2SO_4 and evaporating of the ether, crude hydroxyldiacetal was obtained. Without distillation, it was added to 200 ml of 10% H_2SO_4 solution and it was distillated in steam. After extracting with ether of the distillate, *E*-hex-2-en-1-al (31 g) was obtained, bp. 57–60 °C/35 mm, $n_D^{16.7}$ 1.4461.

ii) *Z,E*-hex-2-en-1-al

Oxidation of *Z*-hex-2-en-1-ol by MnO_2. Under cooling at 0 °C, activated MnO_2[10] (220 g) was added to *Z*-hex-2-en-1-ol[1] (10 g; 0.1 mole) in 300 ml of absol. ether. After stirring for 6 hr, N_2 gas was bubbled into the reaction mixture and under stream of N_2 the oxidation product was quickly filtered off. After evaporating ether in vacuum at room temperature, the two geometrical isomers of hex-2-en-1-al were obtained. The oxidation products were identified with authentic compounds by gas chromatography; isomer ratio *Z*/*E*=53.2/46.8, yield; 6.5 g; 65%.

2. General procedure for Irradiation

0.1 M ether solution of the substrate was irradiated using a 100 W high-pressure mercury lamp with a quartz cooling jacket at room temperature. During irradiation, N_2 gas was bubbled throuh the solution in a closed circulating system. After the irradiation, the ether was evaporated under cooling and bubbling of N_2 in vacuum. The irradiation product was identified with the authentic compounds[4] by gas chromatography.*

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* G. C. G.: PEG-20M; 60 cm, Temp. 100°C, He: 88 ml/min. Retention time of each isomers: *Z*-2-en-: 4.6 min, *E*-2-en-: 5.1 min, *Z*-hex-3-en-1-al: 3.3 min.